

Thermoacoustical Analysis of Polymer Dextran at Different Frequencies

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Abstract. In recent years, measurement of ultrasonic velocity is helpful to interpret solute-solute, solute-solvent interaction in aqueous medium. The ultrasonic speed (U), density (ρ) and viscosity (η) at 313 K have been determined using ultrasonic interferometer at four different frequencies *i.e.* 1, 5, 9 and 12 MHz, pycnometer and Ostwald's viscometer of dextran in aqueous medium respectively. All the three measurements were carried out in a water bath of constant temperature with an uncertainty of $\pm 0.1^\circ\text{C}$. The derived acoustical parameters such as free volume (V_f), internal pressure (π_i), absorption coefficient (α), molar sound velocity (\mathbf{R}) and molar sound compressibility (\mathbf{W}) have been determined from experimental data. The outcomes are described in terms of molecular interaction between the solution components.

KEY WORDS: Aqueous dextran, density, viscosity, velocity, and acoustic parameters.

1 Introduction

In determining the molecular structure and molecular properties of different solutions, there are many physical methods that play significant roles. The progress in ultrasonic technique has become a powerful tool in recent years in analyzing knowledge about the physical and chemical behavior of liquid molecules [1–3]. The ultrasonic analysis of liquid mixtures made up of polar and non-polar components is of greater significance in understanding the intermolecular interaction between the molecules of components and they find many applications in industrial and technical processes.

In this study, U , η and ρ values of aqueous dextran over the concentration percent ranges like 0.1, 0.25, 0.50, 0.75 and 1 have been measured and reported at 1, 5, 9 and 12 MHz at 313 K temperature. The other thermodynamic parameters

like free volume (V_f), internal pressure (π_i), absorption coefficient (α), molar sound velocity (\mathbf{R}) and molar sound compressibility (\mathbf{W}) are also evaluated and reported. The variation of these parameters with concentration and frequency of the solution are studied in terms of molecular interaction between molecules of the solution. Studies in predicting the nature and frequency of molecular interaction in the liquid medium have proved to be enormous.

Dextran is a α -D-1, 6-glucose connected glucan with side chains-3 linked to the spine units of the polymer [4, 5]. We have chosen a polymer dextran as a solute with distilled water as a solvent. This is the only polymer which is water soluble. It has involved a different region of examinations by analysts due to its flexible pharmaceutical, biomedical and modern application [6–9].

2 Experimental Section

2.1 Materials and methods

The aqueous solution dextran of 70,000 Da is prepared according to reported method [10]. The ρ and η of the solution were measured by using pycnometer and Ostwald viscometer respectively, it was filled with required solution and kept in a temperature controlled water bath. The ultrasonic velocity was measured by ultrasonic interferometer operating at various frequencies 1 to 12 MHz [11].

3 Theoretical Aspect

The ultrasonic velocity is determine by [12]

$$U = \lambda \times \nu, \quad (1)$$

where ν is the frequency of the generator which is used to excite the crystal.

The density was estimated using the equation

$$\rho_2 = \frac{w_2}{w_1} \rho_1, \quad (2)$$

where w_1 stands for the weight of distilled water, w_2 – the weight of investigational solution, ρ_1 – the density of water, ρ_2 – the density of investigational solution.

The viscosity was calculated using the equation

$$\eta_2 = \eta_1 \left(\frac{t_2}{t_1} \right) \left(\frac{\rho_2}{\rho_1} \right), \quad (3)$$

where η_1 stands for the viscosity of distilled water, η_2 – the viscosity of solution, ρ_1 – the Density of distilled water, ρ_2 – the Density of investigational solution, t_1 – the time of flow of water, t_2 – the time of flow of investigational solution.

The thermoacoustic parameters U , η , ρ were measured at various concentrations and frequencies. The various acoustical parameters like V_f , π_i , α , \mathbf{R} and \mathbf{W} were calculated from U , η , ρ values using standard formulae [13].

3.1 Free volume

Free volume (V_f) in terms of ultrasonic speed (U) and the viscosity (η) of fluid is as follows:

$$V_f = \left(\frac{M_{\text{eff}} U}{K \eta} \right)^{3/2}, \quad (4)$$

where M_{eff} is the effective molecular weight of the mixture ($M_{\text{eff}} = \sum m_i X_i$, where m_i and X_i are the molecular weight and mole fraction of individual constituents respectively), K is the temperature independent constant which is equal to 4.281×10^9 for all fluids.

3.2 Internal pressure

It can be calculated using the relation as given below:

$$\pi_i = bRT \left(\frac{k\eta}{U} \right)^{3/2} \left(\frac{\rho^{2/3}}{M_{\text{eff}}^{7/6}}, \right) \quad (5)$$

where b represents for cubic pressing, which is thought to be 2 for all fluids, k is a dimensionless consistent free of temperature and nature of fluids. Its value is 4.281×10^9 . T is the absolute temperature in Kelvin, M_{eff} is the effective molecular weight, R is the universal gas constant, η is the viscosity of solution in Ns m^{-2} , U is the ultrasonic speed in m/s , and ρ is the density in kg/m^3 of solution.

3.3 Absorption coefficient / attenuation coefficient

It is a characteristic of the medium. It relies upon the outer condition like temperature, pressure and frequency of estimation. It is given by the formula

$$\alpha = \frac{8\pi^2 \eta f^2}{3\rho U^3}, \quad (6)$$

where f is the frequency of ultrasonic wave.

3.4 Rao's constant

Rao has established the empirical relation between molecular weight, density and ultrasonic speed of fluids as

$$\mathbf{R} = \frac{M_{\text{eff}}}{\rho} U^{1/3}. \quad (7)$$

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This equation is called Rao's equation and \mathbf{R} is also called as the molar sound speed, Rao provided a theoretical explanation of his Rao's equation based on phase rule and the kinetic theory of fluids.

3.5 Wada's constant

Wada had analyzed the variation of molar compressibility with concentration for some fluid systems. He derived the empirical relation

$$\mathbf{W} = \frac{M_{\text{eff}}}{\rho} \beta^{-1/7} . \quad (8)$$

4 Results and Discussion

The experimental values of ρ , η , and U at 313 K for frequencies 1, 5, 9, and 12 MHz for aqueous dextran were used to calculate the acoustical parameters and relevant data are presented in Tables 1–4 and displayed graphically in Figures 1–12.

Table 1. Values of ρ and η of aqueous dextran at 313 K

	Concentration				
	0.10%	0.25%	0.50%	0.75%	1%
ρ [Kg/m ³]	993.5	994.23	995.00	996	997.00
$\eta \times 10^{-3}$ [Ns/m ²]	0.686	0.702	0.739	0.773	0.809

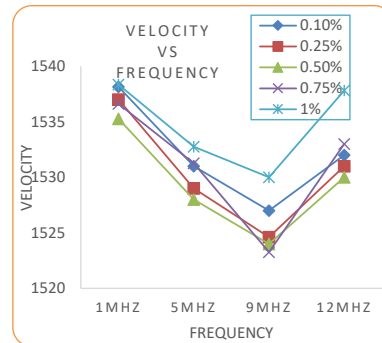
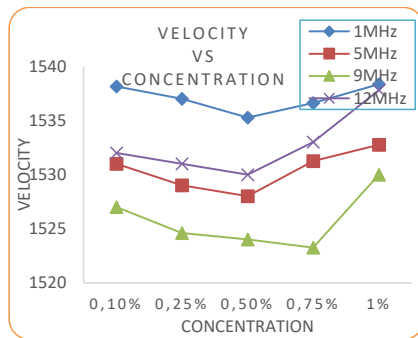


Figure 1. Variation of U with concentration.

Figure 2. Variation of U with frequency.

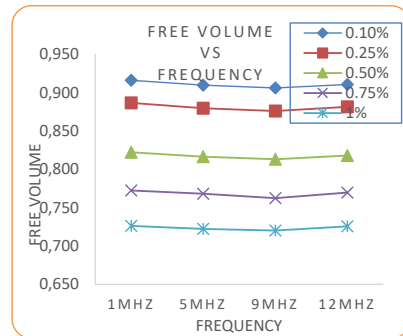
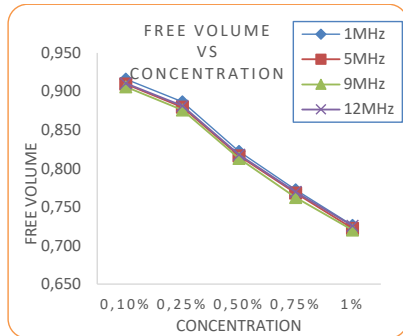


Figure 3. Variation of V_f with concentration.

Figure 4. Variation of V_f with frequency.

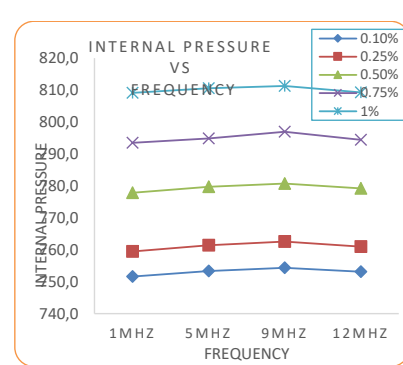
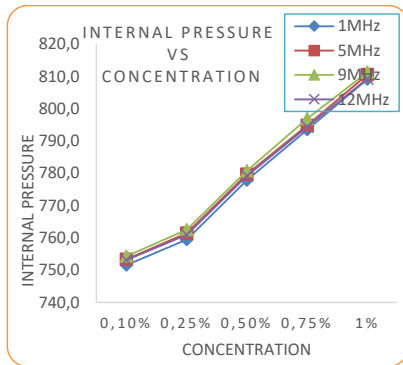


Figure 5. Variation of p_i with concentration.

Figure 6. Variation of p_i with frequency.

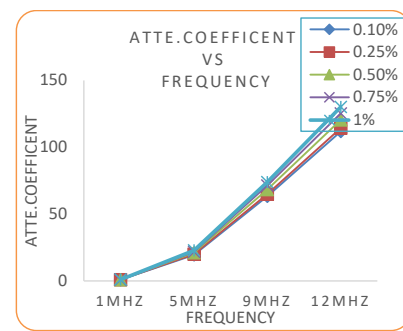
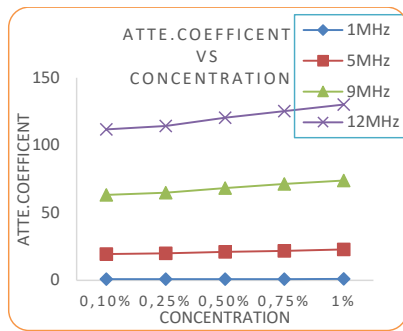


Figure 7. Variation of α with concentration.

Figure 8. Variation of α with frequency.

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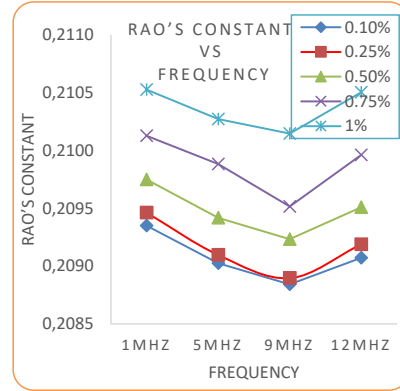
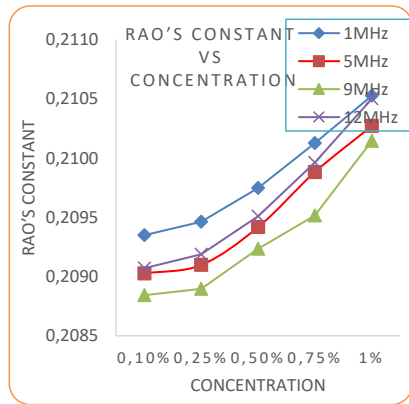


Figure 9. Variation of **R** with concentration. Figure 10. Variation of **R** with frequency.

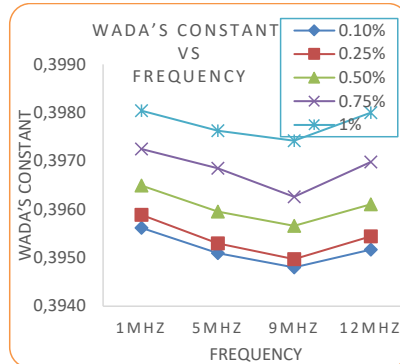
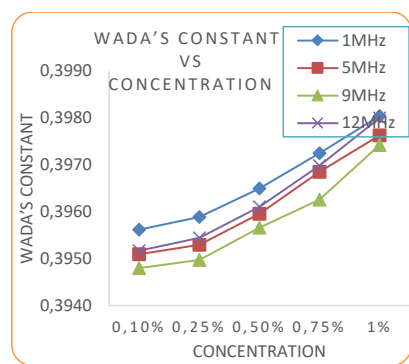


Figure 11. Variation of **W** with concentration. Figure 12. Variation of **W** with frequency.

Table 2. Values of U and V_f of aqueous dextran at 313 K

Concentration	U [m/s]				$V_f \times 10^{-3}$ [m ³ /mol]			
	1 MHz	5 MHz	9 MHz	12 MHz	1 MHz	5 MHz	9 MHz	12 MHz
0.10%	1538.13	1531.00	1527.00	1532.00	0.916	0.910	0.906	0.911
0.25%	1537.00	1529.00	1524.60	1531.00	0.887	0.880	0.876	0.881
0.50%	1535.27	1528.00	1524.00	1530.00	0.822	0.816	0.813	0.818
0.75%	1536.60	1531.25	1523.25	1533.00	0.772	0.768	0.762	0.770
1%	1538.33	1532.75	1530.00	1537.80	0.726	0.722	0.720	0.726

Table 3. Values of π_i and α of aqueous dextran at 313 K

Concen- tration	$\pi_i \times 10^3$ [N/m ²]				$\alpha \times 10^6$ np/m			
	1 MHz	5 MHz	9 MHz	12 MHz	1 MHz	5 MHz	9 MHz	12 MHz
0.10%	751.6	753.3	754.3	753.1	0.769	19.409	63.214	111.648
0.25%	759.4	761.4	762.5	760.9	0.787	19.890	64.815	114.266
0.50%	777.8	779.7	780.7	779.2	0.830	20.954	68.247	120.378
0.75%	793.4	794.8	796.9	794.4	0.866	21.806	71.396	125.316
1%	809.1	810.5	811.3	809.2	0.903	22.736	73.929	130.100

Table 4. Values of **R** and **W** of aqueous dextran at 313 K

Concen- tration	R (m ³ /mole)(m/s) ^{1/3} (10 ⁻³)				W (m ³ /mole)(N/m ²) ^{1/7} (10 ⁻³)			
	1 MHz	5 MHz	9 MHz	12 MHz	1 MHz	5 MHz	9 MHz	12 MHz
0.10%	0.2093	0.2090	0.2088	0.2091	0.3956	0.3951	0.3948	0.3952
0.25%	0.2095	0.2091	0.2089	0.2092	0.3959	0.3953	0.3950	0.3954
0.50%	0.2097	0.2094	0.2092	0.2095	0.3965	0.3960	0.3957	0.3961
0.75%	0.2101	0.2099	0.2095	0.2100	0.3972	0.3969	0.3963	0.3970
1%	0.2105	0.2103	0.2101	0.2105	0.3980	0.3976	0.3974	0.3980

It is observed that, although U rises with rise in concentrations at a particular frequency, it gradually decreases at initial concentrations like 0.1, 0.25 and 0.50%. This is due to the structural changes in the polymer solution which lead to an increase in intermolecular forces. Further, U decreases with frequency from 1 to 9 MHz for a given concentration and temperature. Such a velocity decrease is an indicator of the presence of a weak molecular interaction between the liquid and the solvent. However, the situation is reversed when the frequency is high (12 MHz), which may be due to thermal agitation [14].

It is observed that V_f and π_i in general expected to show a reverse trend with each other in both concentration and frequency, which leads to association of atoms of the component liquids with change in concentrations. Whereas the variation of frequencies in both V_f and π_i are almost parallel (Figure 4 and Figure 6) to frequency axis. This conforms that there are little variations of these parameters with respect to frequencies where cohesive force does not affect the system [15].

It is observed that α gradually rises with rise in concentrations at higher frequency and the effects are negligible at low frequencies. The trends are parallel to concentration axis that indicate gradual increase in interaction with a rise in the concentration. As frequency rises, α rapidly rises and interaction decreases [16].

The calculated values of dextran solution of different concentrations for **R** and **W** show increasing trends with concentration as the availability of more components in a given region result in the medium becoming tightly packed and thus

increasing interaction. Furthermore, it is needless to claim that as concentration increases, more mass is produced in the solution components rather than the enlargement of the size. Figure 10 and Figure 12 highlight that there is presence of small complex formation at low frequency and the complex formation becomes weak at higher frequency due to agitation of the molecules [17, 18].

5 Conclusions

Ultrasonic speed, density and viscosity have been measured for aqueous dextran solution at different frequencies in constant temperature. When the concentration increases, more and more solute molecules move closer to the solvent molecules and thereby increasing the solute-solvent interactions. This is a clear indication of intermolecular interactions because of hydrogen bonding of aqueous dextran solution. The method of studying the molecular interaction from the knowledge of variation of thermodynamic parameters with concentration and frequencies gives an insight into the molecular process. Industry demands reliable data on the physical and chemical properties of a wide variety of liquid solutions.

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